

Sequestration of atmospheric carbon dioxide as inorganic carbon in the unsaturated zone under semi-arid forests

Israel Carmi^{a,*}, Joel Kronfeld^a, Murray Moinester^b

^a Department of Geosciences, Tel Aviv University, 69978 Tel Aviv, Israel

^b School of Physics and Astronomy, Tel Aviv University, 69978 Tel Aviv, Israel

ARTICLE INFO

Keywords:

Carbon dioxide sequestration
Unsaturated zone
Semi-arid region

ABSTRACT

Inorganic carbon, as allogenic and pedogenic carbonates mixtures, can be a significant component of arid and semi-arid zone soils. It has been claimed, that the formation of pedogenic carbonates does not sequester atmospheric carbon dioxide, when formed from the preexisting limestone: $\text{Ca}^{+2} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}$. But if the cation is derived from a non-carbonate source sequestration can occur. Among the unconsidered sources in nature are the contribution of Ca^{+2} , released from adsorption sites on the clay surfaces. Analysis of DIC, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ data show in the present study that sequestration does occur within the unsaturated zones (USZ) in a semiarid region: 1) the DIC is depleted as carbonate precipitates into the USZ, 2) the released CO_2 , does not immediately return to the atmosphere (except for the samples nearest to the surface) but recycles to the soil-gas of high CO_2 partial pressure, and 3) that radiocarbon, which is generated only in the overlying atmosphere, and exhaled into the USZ by roots and the decay of soil organic matter, is incorporated within the calcite mineral. Thus, a net sequestration of atmospheric CO_2 does occur.

1. Introduction

1.1. Atmospheric CO_2 and sequestration in the USZ

The carbon dioxide concentration in the atmosphere has risen from approximately 280 ppmv (Craig and Keeling, 1963) to approximately 405 ppmv at present (ProOxygen, 2017) due to burning of fossil carbon (coal and oil). Halting or reducing the increase in atmospheric CO_2 is currently being investigated (Linnér and Wibeck (2015)). One possibility is to utilize photosynthesis to abstract atmospheric CO_2 as Above-ground Biomass Carbon (ABC) and in roots (Kell, 2012; Tans and Wallace, 1999; Watson et al., 2000). Thus, almost 4 billion tons of ABC has been stored since 2003 by tree planting in northern China, equaling 25% of its annual fossil fuel emissions (Liu et al., 2015). Trees, having a finite life time, are temporary carbon stores in terms of centuries only. In temperate zones forestation may compete with agriculture (Martin et al., 2001) resulting in the cutting of food production (Boysen, 2015). Investigated here is the proposal to sequester atmospheric carbon dioxide through afforestation in semi-arid regions as inorganic pedogenic carbonate beneath the ground surface within the unsaturated zone (USZ). Semi-arid regions have marginal agriculture, but indigenous flora (trees and shrubs with deep roots) can be sustained by the 250–600 mm of annual rainfall. In semi-arid regions, the unsaturated

zone (USZ), which extends from the land surface downwards to the water table, is quite thick.

Whereas in temperate regions the rooting depths of coniferous and deciduous forests are ~ 2.8 m, in drier areas, plants sink roots much deeper to reach water. For example, roots of the Shepherd's tree (*Boscia albitrunca*) and the Acacia can exceed 60 m in the Kalahari of Africa, while the Israeli Tamarisk (*Tamarix aphylla*) can send its roots down 20 m (Canadell et al., 1996). The process of long term storage of inorganic carbon below the ground surface has generally been neglected. CO_2 released through roots, combined with bacterial oxidation of soil organic matter, can generate soil CO_2 partial pressures orders of magnitude higher than that in the overlying ambient atmosphere (e.g. Carmi et al., 2013; Clark and Fritz, 1997; Pumpanen et al., 2008). Some of this gas diffuses upwards and leaves the soil (Carmi et al., 2015). The rest can interact with soil moisture: the high partial pressure of CO_2 forms dissolved inorganic carbon (DIC), which later combines with bivalent cations and precipitates as pedogenic carbonate within the USZ. Where rainfall is plentiful, this precipitate dissolves. In semi-arid regions, where rainfall is sparse, precipitated calcite (pedogenic carbonate) can remain stable for thousands of years (Cerling, 1984). The pedogenic carbonate formed in the USZ and the bicarbonate (DIC) together comprises sequestered inorganic carbon.

* Corresponding author.

E-mail address: carmiisr@post.tau.ac.il (I. Carmi).

<https://doi.org/10.1016/j.catena.2018.09.042>

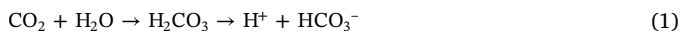
Received 2 November 2017; Received in revised form 16 September 2018; Accepted 22 September 2018

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1.2. Theoretical considerations of the role that inorganic carbon plays in the sequestration of atmospheric CO₂ in the USZ

Soils are a considerable, neglected sink for organic and inorganic carbon (e.g. Schlesinger, 2000). Monger (2014) presents several cogent reasons for this contention. Foremost, he believes that for pedogenic carbonate to be a net sink, the calcium ions must come from silicate weathering, or some other non-carbonate source. Moreover, he points out that it is technically difficult to readily determine the ratio of lithogenic to pedogenic carbonate in a soil. Soil inorganic carbon can be of two basic origins, with different relevancy as to their ability to abstract and store atmospheric carbon. Lithogenic carbonates, primarily marine limestone, were formed in the distant past and bear no relationship to the present atmosphere. Pedogenic carbonate is authigenic, formed within the soil profile as dissolved inorganic carbon (DIC) combines with calcium cations in the soil moisture, eventually precipitating. Trees and shrubs inhale atmospheric carbon dioxide for photosynthesis and exhale some of it through their roots into the unsaturated zone of the soil. The partial pressure of the CO₂ in the soil gas is much greater than that of the ambient atmosphere. A series of fractionation stages (e.g., Clark and Fritz, 1997, p.120) affect the carbon isotopic ratios through the various steps that start with the exhalations of C3-type plants, which dominate in the study areas (Vogel et al., 1986), and transforms the CO₂ (g) to the solid carbonate precipitate. Here, calcium will be taken to represent all of the other cations, (e.g. iron and magnesium) that can form carbonate minerals. It should be noted that while the isotopic difference between the sediment and the atmosphere is slight for ¹³C (on the order of 1%), it is 100% for radiocarbon. The host sediment initially contains no ¹⁴C, which is created in the upper atmosphere.

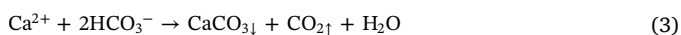
The chemical equations for the process of the dissolution of the soil gas into the soil moisture, the formation of carbonic acid and the precipitation of calcite can be presented in simplified form as:



Soil CO₂ combines with the soil moisture to form a carbonic acid solution which rapidly dissociate to H⁺ and HCO₃⁻ (or CO₃²⁻ depending upon the pH [Clark and Fritz, 1997, p.116]). In this reaction, atmospherically derived CO₂ becomes bicarbonate (DIC), generally the most common anion of ground water (Kronfeld et al., 1993; Rogojin et al., 2002). The dissolution reaction (Eq. (1)) is comparable to carbon sequestration, as the source is atmospheric CO₂ (e.g., Suarez, 2000; Drees et al., 2001; Monger et al., 2015).



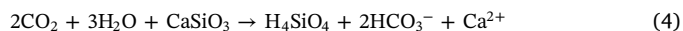
The carbonic acid, formed in Eq. (1), can dissolve existing calcite (dominantly limestone) within the soil to release calcium ions. The HCO₃⁻ in Eq. (2) is from relic carbonate, not related to modern atmospheric CO₂. This HCO₃⁻ does not therefore sequester modern atmospheric CO₂.



The cations released in Eq. (2) combine with the DIC. Facilitated by various processes principally degassing of CO₂ or the evaporation of H₂O, secondary calcite precipitates. Rate limiting factors for the formation of secondary carbonate include the abundance of Ca²⁺, and the partial pressure of CO₂. However, Eq. (3) would imply that no atmospheric CO₂ is sequestered, if for every mole of calcite formed, 1 mol of CO₂ returns to the atmosphere. Thus, it has been assumed (e.g., Monger et al., 2015) that the formation of pedogenic carbonate is neutral as to atmospheric carbon abstraction and storage. However, when this reaction occurs within the USZ soil column, which is generally thick in semi-arid regions, only the topmost fraction is in direct contact with the atmosphere. Though this may be considered to be an “open system”, the rate of release of the gas is limited by diffusion. Much of the CO₂ released by Eq. (3), particularly from precipitation occurring at depth,

should be expected to enter and mix with the relatively high partial pressure CO₂ in the USZ soil-gas.

If there are non-carbonate sources of supply of calcium ions, net atmospheric CO₂ sequestration will occur. Wollastonite is used here as a representative calcium silicate mineral for illustrative purpose in Eq. (4).



In the weathering of silicates, all of the CO₂, unlike in carbonate weathering is derived ultimately from atmospheric CO₂. In this representative reaction, 2 mol of atmospherically derived CO₂ are used to produce 2 mol of HCO₃⁻ but only 1 mol of CO₂ is liberated when these 2 mol combine with Ca²⁺ to precipitate CaCO₃. A net sequestration of atmospheric CO₂ therefore unambiguously occurs. A variety of sources of calcium ions, outside silicate weathering or from relic limestone, are present in nature. Moreover, if there are other sources of calcium in the sediment, which can be adsorbed as a cation on the surface of admixed clay minerals, weathered feldspar, or gypsum, sea spray or rain, then there may be net sequestration of atmospheric CO₂ when Ca²⁺ combines with HCO₃⁻ (Eq. (1)) to precipitate calcite. It is important therefore to evaluate for sequestration under the field conditions rather than theoretical or laboratory conditions. Singer (2007) has shown that the dominant adsorbed cations on the clays of Israel are calcium and magnesium. Moreover, these cations are readily amenable to being replaced by H⁺ ions from carbonic acid (Eq. (1)). For areas relatively close to the sea the cations may be introduced by sea spray and rain. Loewengart (1961) has shown that aerosols derived from sea spray are the major source of salinity for rainwater recharge in Israel.

Three previous field studies in Israel indicated that precipitation within the USZ is occurring and that there is a net transfer of atmospheric CO₂ when calcite is precipitated (Carmi et al., 2009, 2013, 2015). The primary purpose of these investigations was to study the evolution of carbon isotopes as carbon (in the gas, liquid and solid phases) traverses the USZ to the water table. These studies are now revisited with the addition of some new data from a shallow core (Table 1) for they provide a new perspective as to whether or not there is a net storage of atmospheric CO₂ within the soil profile as pedogenic calcite.

2. Nizzanim and Yatir sampling sites reconsidered in view of the inorganic sequestration of atmospheric CO₂

2.1. Sampling sites

Two sampling sites, both within the semi-arid zone, were studied. The first was located in the USZ above the Coastal Plain aquifer within the non-irrigated Nizzanim Nature Reserve (GPS: 31.773016, 34.655555). The flora is deep-rooted sycamores and retamas, and various shallow seasonal plants. The sediment is composed of quartz, clay, and carbonate with occasional additions from dust storms. The other sampling site was located in the Yatir Forest (GPS: 31.347129, 35.050898), situated above the carbonate Mountain Aquifer at an elevation of ~650 m above sea level, along the southwestern flanks of the Judean Hills. Beginning in 1966, the Jewish National Fund planted 28 km² of trees at Yatir at an average spacing of 3 m. The topsoil is rather shallow and is composed of loess, mostly quartz, with carbonate minerals and clays, as well as a lesser percentage of feldspar minerals. This eolian deposit, transported from the Sahara and the Arabian

Table 1
Data from the Yatir Forest shallow soil core profile.

Depth cm	Humidity (%)	DIC (mol CL _{sed} ⁻¹)	δ ¹³ C (‰)	δ ¹⁸ O (‰)
30–60	10.7	4.5	–15.6	0
60–90	12.0	3.4	–14.4	–2

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